

THE EFFECT OF CATALYST, HYDROGEN PRESSURE, AND SOLVENT IN COAL LIQUEFACTION UNDER SIMULATED PREHEATER CONDITIONS

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INTRODUCTION

The purpose of a preheater in a coal liquefaction plant is to raise the temperature of a coal slurry to the reaction temperature before entering the reactor chain. In practice, the preheater actually serves as the first reactor because significant chemical and physical changes take place in the coal slurry as it heats to the reaction temperature. Investigations of these changes were carried out at the Fort Lewis and HRI pilot plants.¹⁻³ In addition to the actual preheaters, microautoclave experiments were used to simulate the HRI preheater as well as the preheater at the Wilsonville pilot plant.^{2,4} These studies have shown that much of the conversion of the coal into initial products is complete by the time the slurry exits the preheater.

All of the preheater studies described above were carried out in the absence of dispersed catalysts; the coal did not contact the catalyst until it entered the first packed-bed reactor. In this arrangement, the slurry was at reaction temperature when it contacted a preactivated catalyst. With dispersed catalysts, the catalyst precursor is added to the initial slurry and travels through the preheater with the coal. For the precursor used in this investigation, no work has been performed which shows whether the short time in the preheater is sufficient to form an active catalyst. If the catalyst did activate, would it have any effect on the coal breakdown reactions taking place in the preheater? The purpose of this study was to look at these issues. Microautoclave experiments were employed in which the loadings of coal, solvent, hydrogen, and catalyst were similar to those used in large-scale coal liquefaction preheaters and in which the heat-up was performed in a manner that reasonably approximated the time/temperature histories of the large units. In addition to routine microautoclave liquefaction product characterization procedures, extraction with N-methyl-pyrrolidone and thermogravimetric analysis were used to gain more insight into the reactions occurring as coal dissolves and begins to liquefy.

EXPERIMENTAL

The reactor used in these experiments was a previously described microautoclave system modified to allow controlled submersion of the reactor into the heated sand bath.⁵ This was accomplished by restricting the airflow to the pneumatic lift on the sand bath. A fairly reproducible internal time/temperature profile was obtained that resembled the available data from the Fort Lewis and Wilsonville pilot plant preheaters. A comparison of these data is shown in Figure 1. The solids concentration of 36.6% and slurry fraction loading of 0.4 used in these experiments were also representative of values used in these preheaters. For the microautoclaves used in these experiments, 7.0 g of coal and 11.0 g of solvent were used. In experiments without solvent, only 7.0 g of coal was placed in the reactor.

The coal used in this study was DECS-17 (Blind Canyon) coal, a bituminous coal from the Penn State Sample bank. The solvent used was a coal-derived vacuum gas oil (VGO) produced by Exxon in its bench-scale coal liquefaction reactor; this material had a boiling range of 274 - 510°C and was 100% soluble in cyclohexane.⁶ The catalyst used in this study was a dispersed MoS₂ formed by the decomposition of Mo(CO)₆ in the presence of H₂S.⁵ The precursor was added at a concentration of 1000 ppm Mo relative to the daf coal in the catalytic experiments. A H₂/3%H₂S gas mixture was used in most experiments at a cold pressure of 7.1 MPa (6.9 MPa hydrogen). One experiment was performed with an equivalent pressure of nitrogen. Also, thermal and catalytic experiments were carried out without solvent at higher (13.8 MPa) and lower (3.4 MPa) hydrogen pressures.

Experiments consisted of filling the reactor then raising the temperature to 425°C, along the profile given in Figure 1, followed by an immediate quench. Several experiments were performed in which the reactor was held at 425°C for 60 minutes following heat-up before being quenched. The products were initially fractionated by sequential extraction with THF and cyclohexane. The THF-insoluble fractions were further fractionated using a modification of published NMP extraction procedures.^{7,8} Small amounts (0.6-0.7 g) of the THF insolubles were refluxed under nitrogen with 90 ml of NMP (BASF) for 1 hour. The solution was centrifuged at

500xg for 60 minutes. The supernatant was collected and the residue resuspended in 90 ml of fresh NMP. The refluxing/centrifugation was repeated 4 times. The combined supernatants were filtered through a 5 μ m Mitrex Teflon filter. The residue was washed onto the filter paper with acetone then the filter cake was washed with water and dried overnight in a vacuum oven. The filtrate was concentrated to about 20 ml volume by rotary evaporation. Acidified water (500 ml of 0.002 N) was then added dropwise overnight with stirring to precipitate the NMP-soluble material. This solution was filtered through a second Teflon filter, which was then washed with acetone and dried overnight in a vacuum oven.

TGA experiments were carried out on the cyclohexane-insoluble, NMP-soluble, and NMP-insoluble fractions using a DuPont 951 TGA. An open quartz pan was suspended from the end of the balance arm and filled with 10-15 mg of sample. The TGA was purged with nitrogen then held at 150°C to remove adsorbed water. The temperature was then raised to 900°C at a rate of 10°C/min. At that point, air was introduced into the TGA and the temperature held at 900°C until a constant weight was achieved. The amount of volatile material in the sample was equal to the weight lost as the sample was heated to 900°C. The weight loss following the introduction of air represented the loss of fixed carbon from the sample through oxidation. The weight of the material remaining in the pan following oxidation was the ash content of the sample. Figure 2 shows a typical curve generated by the TGA from an NMP-insoluble fraction.

RESULTS

The list of experiments, conditions, and conversions is given in Table 1. Cyclohexane, THF, and NMP conversion results are reported on a %daf coal basis. The TGA results for the NMP insoluble fractions are also given in Table 1. Because of the differences in conversions and the presence or absence of catalyst, there are large differences in ash contents of the NMP insoluble fractions. For easier comparisons the percentages of volatile matter and fixed carbon are reported on an ash-free basis.

Catalyst Activation Experiments

The $\text{Mo}(\text{CO})_6$ precursor has been extensively investigated in the microautoclave system. Under slow heat-up conditions (approximately 1 h), hydrogen transfer to the DECS-17 coal was shown by a corresponding increases in THF conversion. This occurred at temperatures as low as 325°C, with a pronounced increase in activity at 370°C.⁵ These experiments were performed without an added solvent, which would tend to mask the effect of the catalyst. Whether similar activation occurs under preheater simulation conditions was addressed by performing both thermal and catalytic experiments, again in the absence of solvent.

Solvent-free/Thermal Experiments The first series of experiments listed in the table are the solvent-free experiments. Hydrogen for the liquefaction reactions could only come from either the coal structure or the hydrogen gas phase in these experiments. Since coal conversion is known to be dependent on the amount of available hydrogen, the results should be dependent on the hydrogen pressure in the reactor if hydrogen gas is used in the reactions. For the thermal case, increasing (JF449) or decreasing (JF451) the hydrogen pressure in the reactor had no effect on conversions over the base pressure experiments (JF412, JF450). The fixed carbon content of the NMP insolubles was also the same in all three cases, further indicating that the reactions taking place are independent of hydrogen pressure. Holding the reactor at the reaction temperature for an additional 60 minutes (JF420) resulted in no additional conversion to NMP soluble material, showing that the initial coal decomposition takes place rapidly. The slower secondary reactions continue to take place during the additional time at reaction temperature with a minor increase in THF conversion and a significant increase in cyclohexane conversion. The fixed carbon content of the NMP insolubles increases as these secondary reactions take place, again showing that hydrogen from the coal structure is used in these reactions rather than gas-phase hydrogen.

Solvent-free/Catalytic Experiments The corresponding set of experiments in which $\text{Mo}(\text{CO})_6$ was included in the reaction show much different results from the thermal set. At the base hydrogen pressure, experiments JF413 and JF447 show greater conversion to NMP, THF, and cyclohexane soluble products compared with the thermal experiments. This immediately indicates that the catalyst precursor has become at least partly active when exposed to only this short heat-up profile. This is important, because it shows that a preactivation step may not be needed for certain dispersed catalysts in large-scale liquefaction processes. The large disparity between the NMP and THF conversions for these two experiments carried out under identical conditions has not yet been resolved.

In addition to determining if the catalyst was activated, the hypothesis that the role of the catalyst was to make gas-phase hydrogen available for the liquefaction reactions was also tested. This was accomplished by performing experiments at both a lower (3.4 MPa, JF448) and a higher (13.8 MPa, JF445) hydrogen pressure. The drastic increases in NMP and THF conversion in going to the higher pressure indicate that this hypothesis is probably correct, but the wide variance in the intermediate pressure experiments must be considered. Even at the lowest pressure, however, the NMP conversion is greater than those found in all thermal experiments.

The presence of the catalyst continues to have an effect on conversions, as seen from the 60-minute catalytic experiment (JF417). The NMP conversion has been affected by the longer reaction time showing a small increase; this was not seen in the thermal experiments. As was seen in the thermal 60-minute experiment, however, there is an increase in the fixed carbon content of the NMP insoluble fraction and greatly increased THF and cyclohexane conversions.

One additional insight can be gained by comparing the TGA results of the thermal and catalytic experiments. The fixed carbon content of the NMP insolubles was $58\% \pm 2\%$ regardless of the amount of NMP conversion. This shows that the volatile matter in the NMP insolubles is not preferentially broken down into soluble product, but that the more condensed structures are equally reactive.

Microautoclave Simulations of a Preheater

The second set of experiments listed in Table 1 are those performed using the VGO solvent. These experiments represent the actual simulations of a liquefaction preheater, where a slurry of coal and a coal-derived solvent are in contact with a hydrogen gas phase as the mixture is pumped through the preheater. In an initial set of experiments, not reported in the table, the VGO was tested under thermal and catalytic conditions without coal present. Elemental analysis, average molecular weights, ^1H NMR, and ^{13}C NMR of the treated and untreated VGO showed no differences, indicating that the VGO itself is not reactive under these conditions. As discussed below, however, there is adduction of the VGO to the coal material in some of the coal plus solvent experiments.

The solvent serves as an additional source of hydrogen for the liquefaction reactions. The dramatic increases in NMP and THF conversions over both the thermal and catalytic solvent-free experiments show how important this source of hydrogen is for these reactions. The importance of having good hydrogen transferring solvents during the heat-up phase of the coal liquefaction process has long been recognized.

Thermal Simulations Thermal experiments were carried out under three sets of conditions in which VGO solvent was used. The baseline preheater simulations (JF410, JF415, JF453, JF455) had an average of 88% conversion to NMP solubles and 68% conversion to THF solubles within the five minute heat-up to 425°C. Cyclohexane conversions for these experiments are lower than those for the solvent free experiments, however. The reason for this is that the amount of VGO present is subtracted out of the cyclohexane solubles collected at the end of the experiment. Some of the VGO solvent adducts to larger molecular weight coal molecules, however, and becomes insoluble in cyclohexane. This type of solvent behavior has been reported before with complex solvents.⁹

Performing the same experiment under 6.9 MPa of nitrogen, with no hydrogen gas present (JF414), produces the same NMP and THF conversions. This again shows that the presence of the hydrogen gas is not important in the thermal experiments. An experiment was also performed holding the coal and solvent at 425°C under 6.8 MPa of hydrogen for 60 minutes following the heat-up (JF459). A disproportionation occurs over time, with retrograde reactions causing a decrease in the NMP conversion while secondary reactions increase the THF and cyclohexane conversions. The cyclohexane conversion, however, remains lower than that achieved in the solvent-free experiments held for 60 minutes due to reaction of the solvent with the coal. The NMP insoluble material is also becoming more condensed, with the fixed carbon content increasing almost 20%.

Catalytic Simulations From the previous solvent-free results, it is presumed that the catalyst makes hydrogen gas more readily available for liquefaction reactions. Interestingly, however, this has no effect on the NMP conversion catalytic preheater simulation experiments (JF452, JF454, JF456). The presence of the solvent alone provides sufficient hydrogen for this phase of coal dissolution. The additional hydrogen provided by the catalyst does increase the THF and cyclohexane conversions. The catalyst, however, does not prevent solvent adduction reactions because the solvent-free experiments had greater cyclohexane conversions. Fixed carbon

contents of the NMP insolubles from the catalytic and thermal experiments are the same, indicating that the presence of the catalyst does not change the amount of hydrogen extracted from the coal structure during the liquefaction reactions.

In the 60-minute experiment with catalyst present (JF460), the retrograde reactions which took place without catalyst are prevented. There remains some use of hydrogen from the NMP insoluble material, because the amount of fixed carbon in this fraction still increases. In terms of conversion relative to the zero-minute experiment, there is a slight increase in the NMP solubles with larger increases in both the THF and cyclohexane solubles when the reaction is continued for 60 minutes.

CONCLUSIONS

This study confirmed two conclusions from earlier preheater and preheater simulation experiments: 1) The initial coal breakdown reactions occur very rapidly, and 2) greater than 90% of the total conversion for a system is achieved in the preheater.

For its own objectives, this study showed that dispersed catalyst precursor added to the slurry becomes active as it passes through the preheater. Experiments under different hydrogen pressures indicate that hydrogen gas does not participate in liquefaction reactions under thermal conditions, but seem to indicate that the molybdenum catalyst makes hydrogen from the gas phase available for these reactions. Hydrogen provided by the solvent is more easily used than hydrogen supplied by the catalyst, but the coal itself remains a significant source of hydrogen.

The use of NMP extraction to determine conversion is a valuable method for analyzing liquefaction results. NMP's ability to solubilize more of the coal material than THF gives insights into the formation and breakdown of this material. Especially important is the fact that no NMP-soluble material is formed above what would be produced in the preheater even after 60 minutes of additional reaction. The occurrence of retrograde reactions is also easily detected by increases in the NMP insoluble material.

The usefulness of thermogravimetric analysis to characterize solid products from the liquefaction reactions is also demonstrated. Determination of the fixed carbon contents showed that volatile material in the insoluble fraction is not preferentially converted to lighter products in the initial reactions. The use of hydrogen from the coal structure in the initial and secondary reactions was also identified through the TGA work.

Further work needs to be performed, first to determine the cause of the large variation between experiments JF413 and JF447, and second to apply this analysis to coals of lower rank, which would be more susceptible to retrograde reactions.

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Table 1
Preheater Simulation Experiments - Conditions and Results

ID	SOLVENT	GAS	COLD	CATALYST	TIME (min)	CONVERSION			NMP INSOLUBLES (daf%)	TGA RESULTS	
			PRESSURE (MPa)	PRECURSOR		Cyclohexane (daf%)	THF (daf%)	NMP (daf%)		Volatile	Fixed
JF412	NONE	H ₂ /3% <i>H</i> 2S	7.1	NONE	0	20.3	35.4				Carbon
JF450	NONE	H ₂ /3% <i>H</i> 2S	7.1	NONE	0	15.1	28.4	44.3	55.7	39.2	60.8
JF451	NONE	H ₂ /3% <i>H</i> 2S	3.4	NONE	0	17.8	29.4	39.6	60.4	39.3	60.7
JF449	NONE	H ₂ /3% <i>H</i> 2S	13.8	NONE	0	14.7	27.6	40.7	59.3	42.9	57.1
JF420	NONE	H ₂ /3% <i>H</i> 2S	7.1	NONE	60	31.8	33.6	40.2	59.8	31.7	68.3
JF413	NONE	H ₂ /3% <i>H</i> 2S	7.1	Mo(CO) ₆	0	22.5	34.1	55.3	44.7	42.8	57.2
JF447	NONE	H ₂ /3% <i>H</i> 2S	7.1	Mo(CO) ₆	0	22.4	45.7	84.6	15.4	44.2	55.8
JF448	NONE	H ₂ /3% <i>H</i> 2S	3.4	Mo(CO) ₆	0	17.6	36.8	50.6	49.4	39.8	60.2
JF445	NONE	H ₂ /3% <i>H</i> 2S	13.8	Mo(CO) ₆	0	22	52.4	81.7	18.3	44.4	55.6
JF417	NONE	H ₂ /3% <i>H</i> 2S	7.1	Mo(CO) ₆	60	47.9	63.5	75.4	24.6	32.6	67.4
JF410	VGO	H ₂ /3% <i>H</i> 2S	7.1	NONE	0	11.7	67	90.3	9.7	45.4	54.6
JF415	VGO	H ₂ /3% <i>H</i> 2S	7.1	NONE	0	7.4	68.9	91.3	8.7	52.0	48.0
JF453	VGO	H ₂ /3% <i>H</i> 2S	7.1	NONE	0	2	58.4	89.6	10.4	50.0	50.0
JF455	VGO	H ₂ /3% <i>H</i> 2S	7.1	NONE	0	4.1	68.6	81.7	18.3	47.4	52.6
JF414	VGO	N ₂	6.9	NONE	0	18.9	66.5	89.5	10.5	49.9	50.2
JF459	VGO	H ₂ /3% <i>H</i> 2S	7.1	NONE	60	24.7	71.4	82	18	32.0	68.0
JF452	VGO	H ₂ /3% <i>H</i> 2S	7.1	Mo(CO) ₆	0	9.2	69.7	84.9	15.1	43.7	56.3
JF454	VGO	H ₂ /3% <i>H</i> 2S	7.1	Mo(CO) ₆	0	13.6	71.4	92.6	7.4	49.7	50.3
JF456	VGO	H ₂ /3% <i>H</i> 2S	7.1	Mo(CO) ₆	0	7.1	73.8	87.9	12.1	48.8	51.4
JF460	VGO	H ₂ /3% <i>H</i> 2S	7.1	Mo(CO) ₆	60	38.4	84.8	91.5	8.5	36.6	63.4

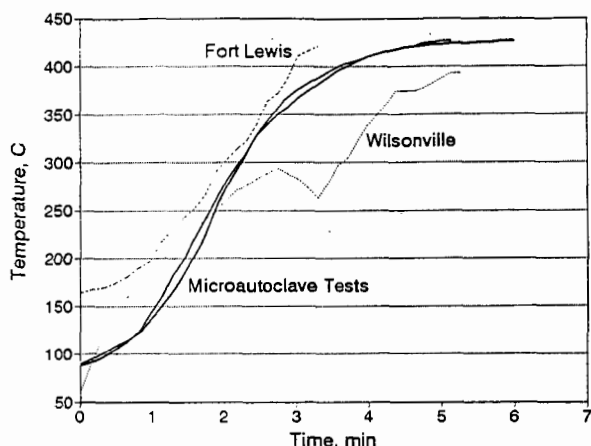


Figure 1. Comparison of microautoclave heating profiles with those from the Fort Lewis and Wilsonville pilot plants.

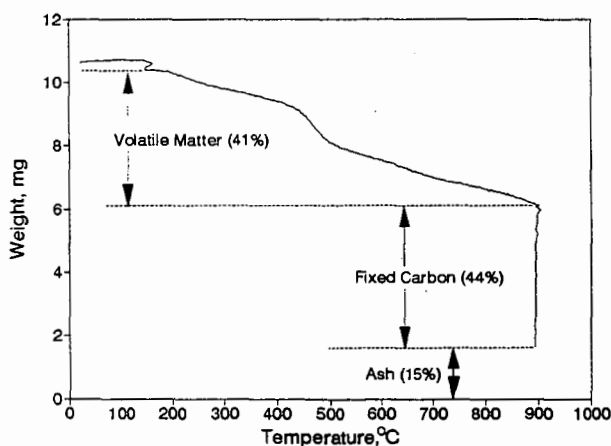


Figure 2. TGA curve of the NMP-insoluble material from experiment JF456 which contained both solvent and catalyst.